DENSIFICATION AND MECHANICAL CHARACTERIZATION OF PURE AND DOPED HYDROXYAPATITE

A THESIS SUBMITTED IN PARTIAL FULFILMENT AS A REQUIREMENT FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

By

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Department of Ceramic Engineering

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Under the Guidance of
Prof. SUDIP DASGUPTA

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CERTIFICATE

This is to certify that the project entitled, **"Densification and mechanical characterization of pure and undoped Hyroxyapatite"** submitted by **Samik Ghosal (Roll No. 109CR0110)** is an authentic work carried out by him under my supervision and guidance for the partial fulfilment of the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of any Degree or Diploma.

Sudip Dasgupta

13.05.13

Prof. Sudip Dasgupta

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ACKNOWLEDGEMENT

I would like to express my heartfelt thanks and gratitude to Professor Sudip Dasgupta, Department of Ceramic Engineering, NIT Rourkela, my guide and my mentor, who was with me during every stage of the work and whose guidance and valuable suggestions has made this work possible. He has been a constant source of inspiration and help, even during troubled times. He has made the effort to be physically present during all stages of synthesis, processing and characterization.

Further, I would also like to thank all the faculty members and staff of Department of Ceramic Engineering, NIT Rourkela for their invaluable support and help during the entire project work.

I would further like to thank all the research scholars, for their round the clock help and support during the entire project work, especially Mr. Kanchan Majhi, Mr. Ganesh Kumar Sahoo, Mr. Sanjay Swain and Miss Geetanjali Parida for their constant help and support.

And finally, my heartfelt thanks to all my friends who have constantly helped me.

Samik Ghosal
109CR0110
10th May, 2013

ABSTRACT

In the present study pure hydroxyapatite (HAp) and 2mol% Mg-doped, Si-doped and Zn-doped hydroxyapatite was processed and their mechanical properties were characterized. Pure and doped Hydroxyapatite powders were synthesized using the wet-precipitation method, using Calcium nitrate ($Ca(NO_3)_2.4H_2O$) and Ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) as precursor materials as a source for calcium (Ca^{2+}) and phosphate ($(PO_4)^{3-}$) ions respectively. Pure HAp powder showed the lowest particle size of 1217 nm as indicated by DLS measurement. XRD study showed the presence of pure HAp phase in all the synthesized powders. Powders were consolidated, sintered at 1250°C for 4 hours and characterized for bulk density, indentation hardness, flexural strength and fracture toughness. Mg-Hap showed the highest bulk density of 2.96g/cc while Zn-Hap showed the highest indentation hardness, fracture toughness and bi-axial flexural strength values of 4.74GPa, 1.49MPa.$m^{1/2}$ and 20.8MPa respectively. It was observed that the doped samples had a higher density, fracture toughness, bi-axial flexural strength and indentation hardness than the pure sample. The results show that doping with suitable cations can ultimately enhance the mechanical properties of hydroxyapatite ceramics.

CONTENTS

CHAPTER 1
INTRODUCTION

1. Introduction

For the past few decades, ceramic materials are increasingly being used for the repair and reconstruction of skeletal diseases and disorders. The term ‘bioceramics’ are used for manmade materials which are used as medical implants and exhibit specific positive response within the body which are aimed for the repair or augmentation of damaged tissue or skeletal parts. Ceramic materials which are biocompatible are called bioceramics[1]. Calcium phosphate ceramics such as hydroxyapatite (HAp) are good candidates for bone substitutes due to their chemical and structural similarity to bone minerals. Nanostructured hydroxyapatite is also expected to have better bioactivity than coarser crystals. Up to 50% of bone by weight is a modified form of hydroxyapatite (known as bone mineral)[2]. Carbonated calcium-deficient hydroxyapatite is the main mineral of which dental enamel and dentin are composed.

Bioactive and bioresorbable phases of calcium phosphate bioceramics are materials of choice for bone–tissue engineering applications because of their similarity of composition with the mineral phase of the bone, excellent biocompatibility, ability to promote cellular functions and expressions, and osteoconductivity. These bioceramics are primarily used as bone substitutes in both dentistry and medicine. Current dental and medical applications of calcium phosphate ceramics or calcium phosphate-based composites include: repair of bone and periodontal defects, maintenance or augmentation of alveolar ridge, ear and eye implants, spine fusion and adjuvant to uncoated implants. These ceramics are used in medical applications because of the range of properties they offer, from tricalcium phosphates being resorbable to hydroxyapatite being bioactive; they are undeniably the current rage for clinical usage. Calcium phosphates exhibit considerably improved biological affinity and activity, compared to other bioceramics. However,

unlike alumina and zirconia these ceramics are mechanically weak and exhibit poor crack growth resistance, which limit their uses to non-load bearing applications such as osteoconductive coatings on metallic prosthesis and as powders in spinal fusion.

Hydroxylapatite, also called hydroxyapatite (HAp), is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO4)_3(OH)$, but is usually written $Ca_{10}(PO4)_6(OH)_2$ to denote that the crystal unit cell comprises two entities. Hydroxyapatite (HAp) has been extensively studied for its exceptional ability in promoting osseointegration as in bone graft substitute and biomimetic coating of prosthetic implants. However poor mechanical properties of HA, in particular its low fracture toughness, has made its widespread adaption in a number of biomedical applications challenging [3].

Previous reports suggest that ion substitution in hydroxyapatite structure is one of the key parameters affecting densification, mechanical and biological properties of HA ceramics. Among different ions used as modifiers, Mg^{2+}, Si^{4+} and Zn^{2+} seem to be very promising.

Our objective was improve the densification kinetics and mechanical properties of sintered HAp compacts by the use of dopants such as Mg^{2+}, Si^{4+} and Zn^{2+} .

Our objective was to improve the densification kinetics and mechanical properties of sintered HAp compacts by the use of dopants such as Mg^{2+}, Si^{4+} and Zn^{2+} . In the present study Mg, Zn, Si ions doped hydroxyapatite (HA) particles were successfully synthesized by introducing 2 mol% of Mg, Zn, Si in the starting solution using wet chemical precipitation method and followed a hydrothermal treatment. The synthesized powders were characterized using powder XRD, FTIR and Dynamic Light Scattering technique for particle size measurement. The

resulting powders were consolidated and sintered at 1250^{o}C for 4 hours. The sintered compacts were characterized for bulk density, micro-hardness, flexural strength and fracture toughness. The effect of dopants on densification and mechanical properties of HAp based ceramics was evaluated.

CHAPTER 2
LITERATURE REVIEW

2. Literature Review

Amongst various ceramics which have been tested for their use inside the human body, calcium phosphate-based ceramics have gained the most attention because of their superior biocompatibility and compositional similarities to bone. However, applications of calcium phosphate-based bioceramics in hard tissue engineering are severely limited by their poor mechanical properties. Currently, these ceramics find applications as coatings, powders, and in particulate forms and are used in repair of maxillofacial and dental defects, drug delivery and as bone fillers[4].

Among different forms of calcium phosphates, the bioactive hydroxyapatite phase has been most extensively researched due to its outstanding biological responses to the physiological environment[5]. However, there is a significant difference of properties between natural apatite crystals found in the bone mineral and the conventional synthetic HAp. Biological apatites are formed in a biological environment through the process of biomineralization and are nano-sized. In addition, the bone mineral also contains trace ions like Na^{+}, Mg^{2+} and K^{+}, Sr^{2+}, Si^{4+} , Cl^{-}, F^{-} , CO_3^{2-} etc. which are known to play a role in overall performance [6]. The influence of ionic substituents in calcium phosphates intended for bone and tooth replacement in biomedical applications is an important research topic, owing to the essential roles played by trace elements in biological processes[7].

A comparative study of bioactivity of synthetic HAp has showed that the promotion of new bone growth onto its surface is not particularly fast as compared with other bioactive materials. Natural HAp does appear to have a higher bioactivity, which has been attributed to the subtle but significant chemical differences found in the structure of HAp. HAp belongs to the apatite group

of minerals, which allow substitutions to take place. These chemical differences are due to the nature of the apatite structure in which a significant number of different ions may be substituted into the structure on a number of different sites. Significant research has been done to improve mechanical performance of calcium phosphate-based bioceramics [8].

Trace ions, particularly Na^{+}, Mg^{2+}, K^{+}, and F^{-}, are well known to be prevalent in the inorganic part of bone[6]. There is a potential for improving the mechanical properties of HAp without altering biocompatibility by introducing small quantities of sintering additives.

Introduction of Mg^{2+} ions has significantly improved the mechanical properties of HAp[8]. Although the basic science explaining favorable behavior of ceramics in the presence of sintering additives has not been explored in every case, scientists have tested numerous sintering additives to improve densification and mechanical properties of various ceramic compositions. The general hypothesis is that sintering additives improve grain boundary properties of ceramics, thereby improving macroscopic properties such as densification, hardness, flexural and compressive strengths[9].

It has been demonstrated that, the resorption of HAp ceramics is quite different from that of bone mineral. Bone mineral crystals are of nano-scale range with large surface areas; therefore, the resorption by osteoclasts is quite homogeneous. Synthetic HAp on the contrary, presents a low surface area and has strong bonding. It has also been shown that the bioactivity of conventional synthetic HAp ceramics is inferior to the bone mineral.

There is a constant need for orthopedic and dental implant formulations that have better osseointegrative properties. It is favorable to incorporate trace ions that are naturally present in

the bone mineral to improve bioactivity of synthetic HAp. It is believed that bone grafts fabricated using nanocrystalline HAp powder doped with essential trace elements would possess superior mechanical and biological properties, analogous to natural bone [8].

CHAPTER 3

EXPERIMENTAL PROCEDURE

3. Experimental Procedure

3.1 Synthesis and Processing of pure and doped hydroxyapatite powder

Wet chemical precipitation route was used to synthesize pure and doped hydroxyapatite powders. Calcium Nitrate $Ca(NO_3)_2.4H_2O$ and Ammonium Dihydrogen Orthophosphate ($NH_4H_2PO_4$) were used as a source of Ca and P respectively. To synthesize Mg, Zn and Si doped hydroxyapatite, magnesium nitrate $Mg(NO_3)_2.6H_2O$, zinc nitrate $Zn(NO_3)_2.6H_2O$ and tetraethyl ortho silicate$(OC_2H_5)_4Si$ were used as a source of Mg, Zn and Si respectively. Ammonium hydroxide was used to adjust the pH of the aqueous solution containing Ca^{2+} and PO_4^{3-} and dopants.

Table 1: Weights of precursor materials for synthesis of pure and doped HAp powder

Sample	**$Ca(NO_3)_2.4H_2O$**	**$(NH_4H_2PO_4)$**	**$Mg(NO_3)_2.6H_2O$**	**$Zn(NO_3)_2.6H_2O$**	**Si $(OC_2H_5)_4$**
Pure HA	13gram	3.79gram	------	-------	------
2 mol% Mg doped HA	12.73gram	3.79gram	0.282gram	-------	------
2 mol% Zn doped HA	12.67gram	3.79gram	-------	0.327gram	------
2 mol% Si-doped HA	12.771gram	3.79gram	-------	-------	0.229gram

100 ml of Ca^{2+} and PO_4^{3-} solution was used to synthesize the above powder. Corresponding amount of dopant was added to 100 ml of Ca^{2+} solution. Two separate solutions of Ca^{2+} and PO_4^{3-} were mixed in a molar ratio of Ca:P (1.67:1),stirred for 30 minutes and then NH_4OH was added to adjust the pH at 10 with constant stirring for overnight. The white gelatinous precipitate appeared which was processed as follows.

3.1.2 Washing

The precipitate has then been washed thoroughly using distilled water by the centrifugal process in Centrifuge machine.

Centrifuge cycle: 8000 rpm for 5 minutes

Each sample has been washed properly for at least 3 times.

3.1.3 Hydrothermal method

Hydrothermal synthesis includes the various different techniques of crystallizing substances from high-temperature aqueous solutions at high vapour pressures. It is also termed as hydrothermal method.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure at a temperature of 250^{o}C. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the

opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.

The solution, after the hydrothermal treatment, is taken and decantation is done to remove most of the water.

3.1.4 Freeze Drying

The next step is freeze drying. It was done using the necessary apparatus. Freeze-drying technique uses the principle of freezing the solvent and then reducing the surrounding pressure to allow the ice surrounding the powder to sublimate directly from the solid phase to the gas phase to get agglomerate free power with uniform particle size distribution.

3.1.5 Processing of HAp compacts

The powder was taken and ground in a mortar pestle. After that, small amounts of powders were taken and weighed. The amount of powder taken for one pellet was 0.8gram. Then, the powder was pressed using a 12mm diameter die, using a load of 5 tons with a dwell time of 30 seconds each to fabricate green hydroxyapatite(pure and doped) compact followed by sintering at 1250^{o}C for 4 hours .

3.2 Characterization

Both as synthesized doped and undoped HA powder as well as sintered pellets were characterized using the following techniques.

3.2.1 Characterization of doped and undoped HA powders.

3.2.1.1 XRD Analysis

The XRD analysis of the powders synthesized was done using Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu Kα radiation (λ = 1.5406 A°) at 40 kV and 30mA and diffraction patterns were recorded over Bragg's angle 2θ range of 20-80^{o}.

3.2.1.2 FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point and this process is repeated many times. Later, a computer takes all this data and works backwards to infer what the absorption is at each wavelength.[10] all the data were taken in the range of 400-4000 cm^{-1}.

3.2.1.3 Particle Size Distribution

Dynamic light scattering is a technique that can be used to determine the size distribution profile of small particles in suspension. Approximately, 0.002 gm of doped and pure HA powder was

added to 50 ml of water at pH-10 and ultrasonicated for 15 min to minimize the degree of agglomeration. The aqueous suspension of HA powders at pH-10 was stable against flocculation for a long time under the influence of strong electric double layer repulsion around the negatively charged particle surface. The particle sizes were automatically determined from the autocorrelation function using the Stokes–Einstein equation: $r = kT/6D\pi\eta$, where r is the particle radius, k is the Boltzmann constant, T is the absolute temperature, D is the diffusion coefficient, and η is the viscosity of the liquid in which the particles were suspended.

3.2.2 Characterization of sintered HAp pellets

3.2.2.1 Bulk Density

The sintered pellets of the composite were immersed in water which was boiled for 3 hours until no vapours are seen coming out of the pellets. Now the dry, soaked and suspended weight of the pellets is calculated. Bulk Density is calculated by the formula:

$$\text{Bulk Density} = \frac{Dry\ Weight}{Soaked\ Weight - Suspended\ Weight}\ x\ Density\ of\ the\ liquid$$

3.2.2.2 Microstructural Analysis

The pellets were observed under the Scanning Electron Microscope for microstructural analysis and calculating the crack length.

3.2.2.3 Vickers Hardness test

The hardness of the pellets was measured by Vickers Hardness Tester.

An indent was given on the pellet and the lens of the instrument was focused on the diameter of the indent.

Vickers hardness is given by the formula:

$HV = 1.854 * F/d^2$

where F is the load of the indent given, measured in (KgF) and d is mean diameter of the indent measured in (mm).

3.2.2.4 Bi-Axial Flexural strength

The diameter and thickness of the pellets were measured. Now the compressive strength of the pellets were measured by UTM machine. Here the pellets are kept on their width and a constant extension per time was fed in the instrument. The instrument measures the maximum load at fracture. Flexural strength is given by the formula:

$F=2P/\pi dt$

where F is the maximum load at fracture, d is diameter of the pellet and t is the thickness of the pellet.

3.2.2.5 Fracture Toughness

Fracture toughness is determined by using the Vickers Hardness, the diagonal length of the indent and the crack length.

$K_{IC}=0.16H_v a^2 c^{-3/2} (MPa.m^{1/2})$

Where a=diagonal length

c=crack length

and H_v=Vickers Hardness(GPa)

CHAPTER 4
RESULTS
&
DISCUSSIONS

4. Results and Discussions

4.1 Results

4.1.1 Phase Identification of the synthesized powders

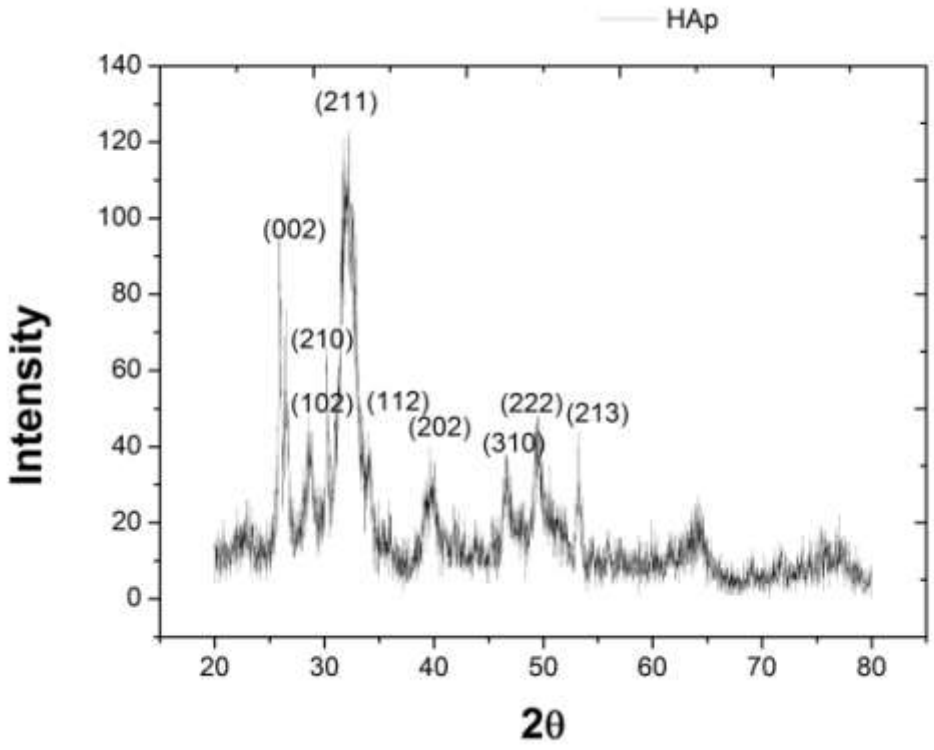

Fig 4.1a XRD pattern of pure HAp powder

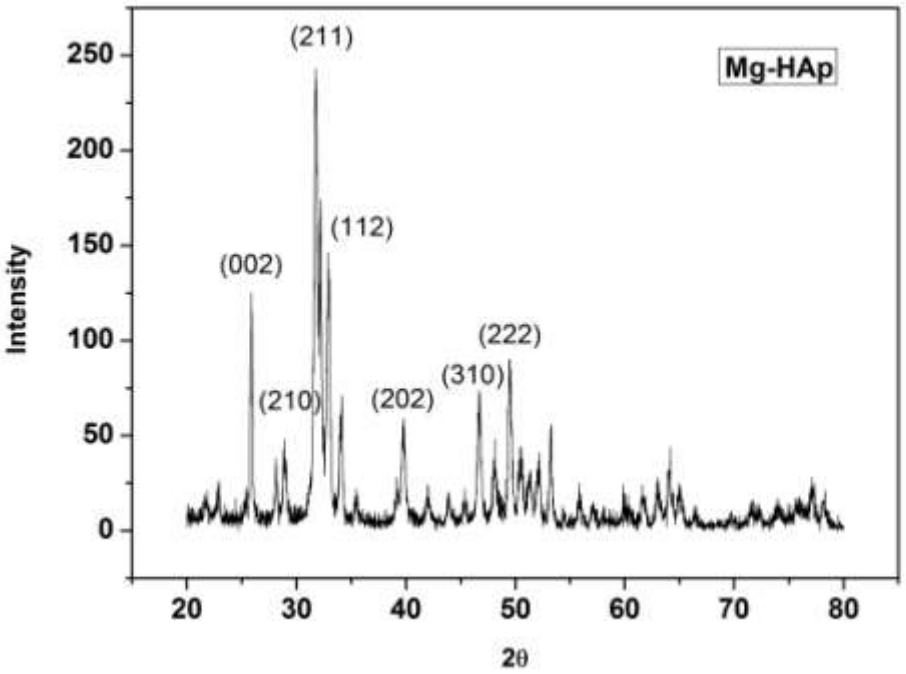

Fig 4.1b XRD pattern of Mg-HAp powder

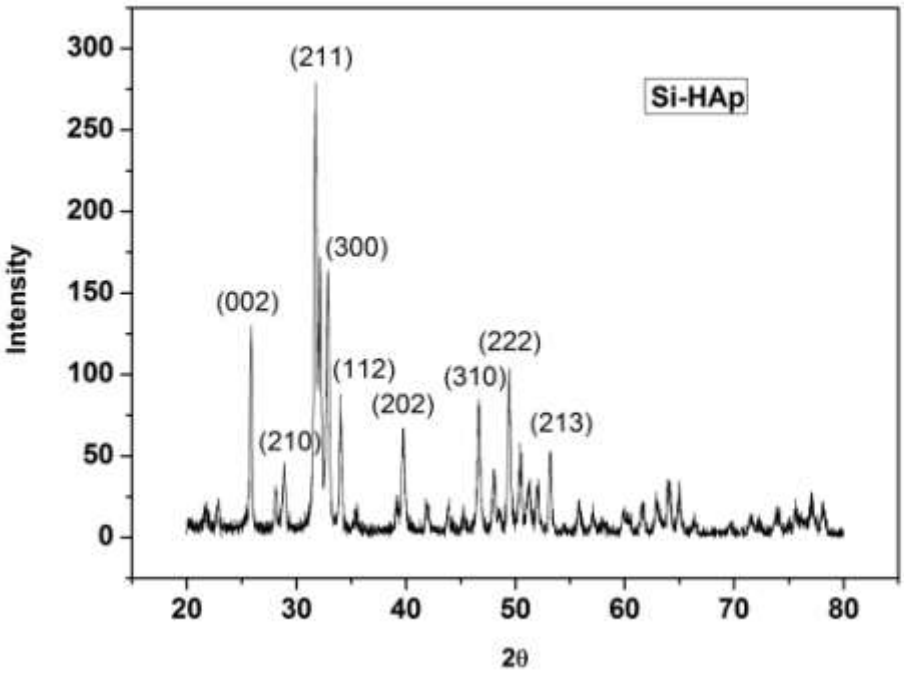

Fig 4.1c XRD pattern of Si-HAp powder

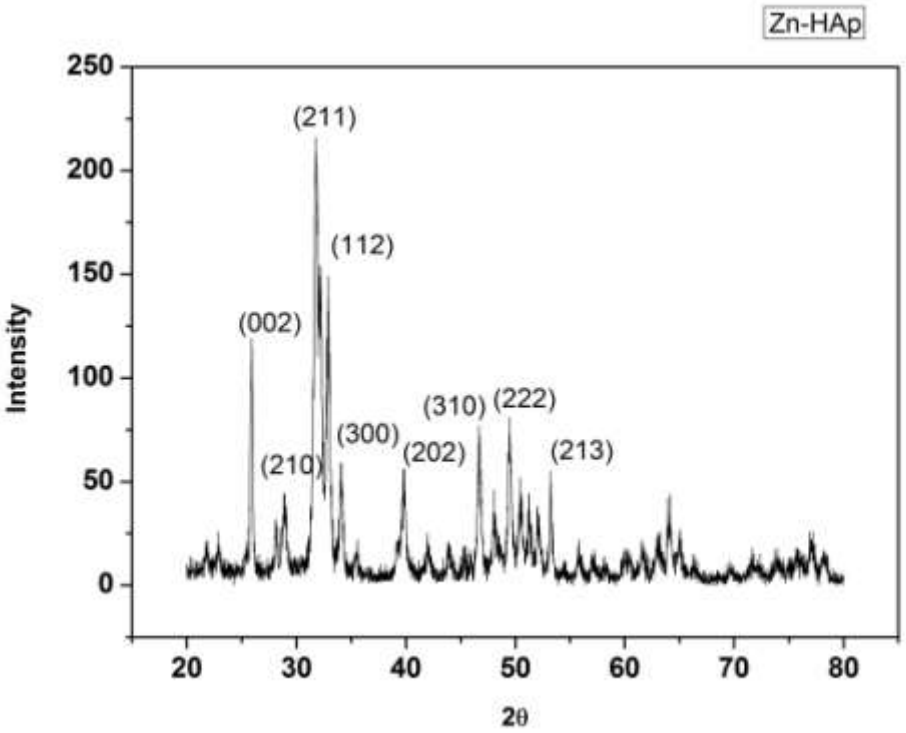

Fig 4.1d XRD pattern of Zn-HAp powder

Figures 4.1a-d show the X-Ray diffraction pattern of as synthesized doped and undoped powder. All the XRD patterns showed the presence of pure HAp phase. Thus, dopant has no effect on the phase composition of synthesized HAp powder. The comparative XRD pattern of pure and doped HAp powders is shown in figure 4.1e which reveals the fact that there is no dissimilar phase in all the synthesized powders.

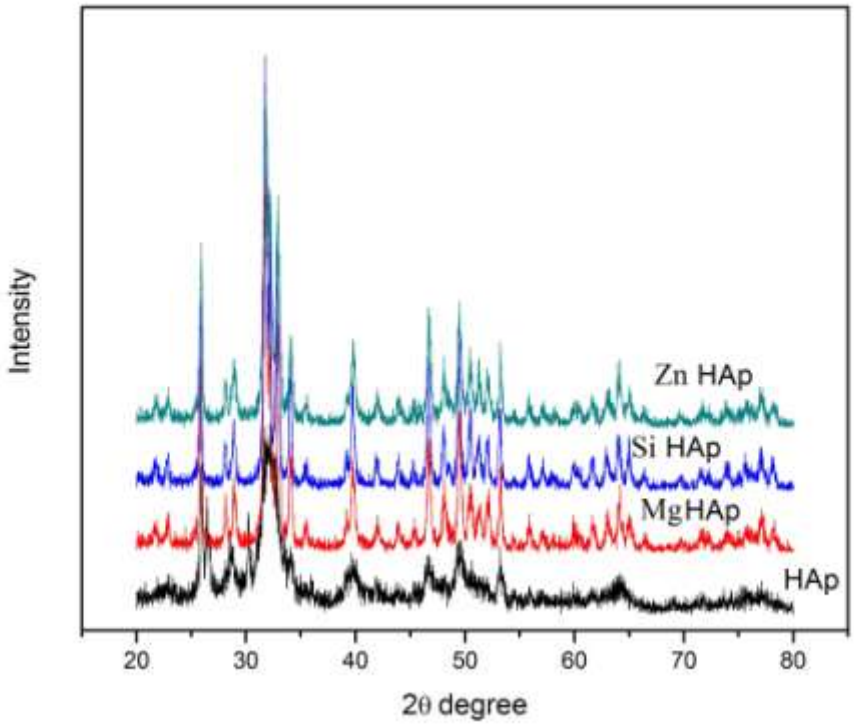

Fig 4.1e X-Ray Diffraction patterns of HAp, Mg-HAp, Si-HAp and Zn-Hap powders

4.1.2 Fourier Transform Infrared Spectroscopy

Figure 4.2 (a,b,c,d) shows the FTIR spectra of pure and doped HAp powders..

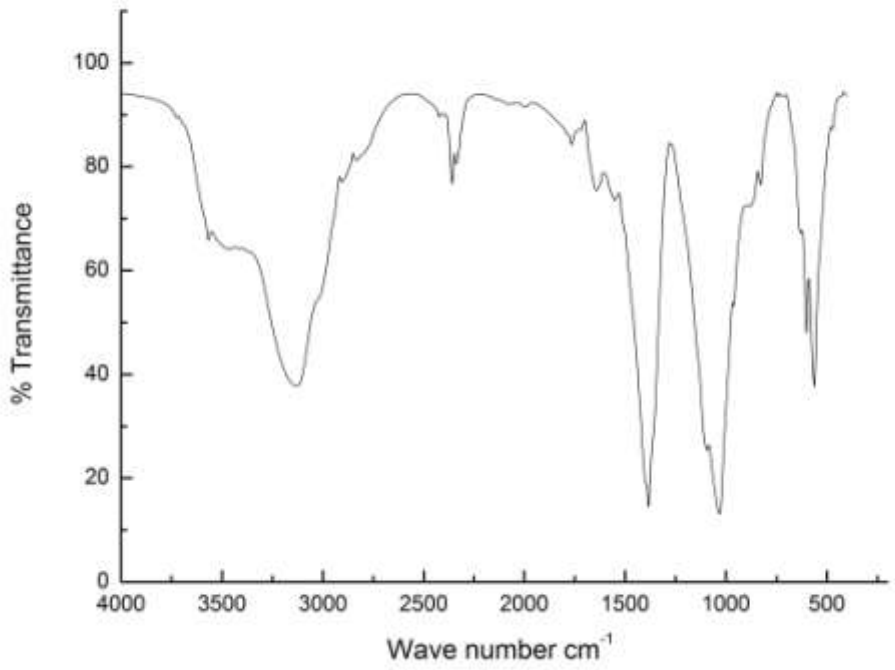

Fig 4.2a FTIR spectra of pure HAp

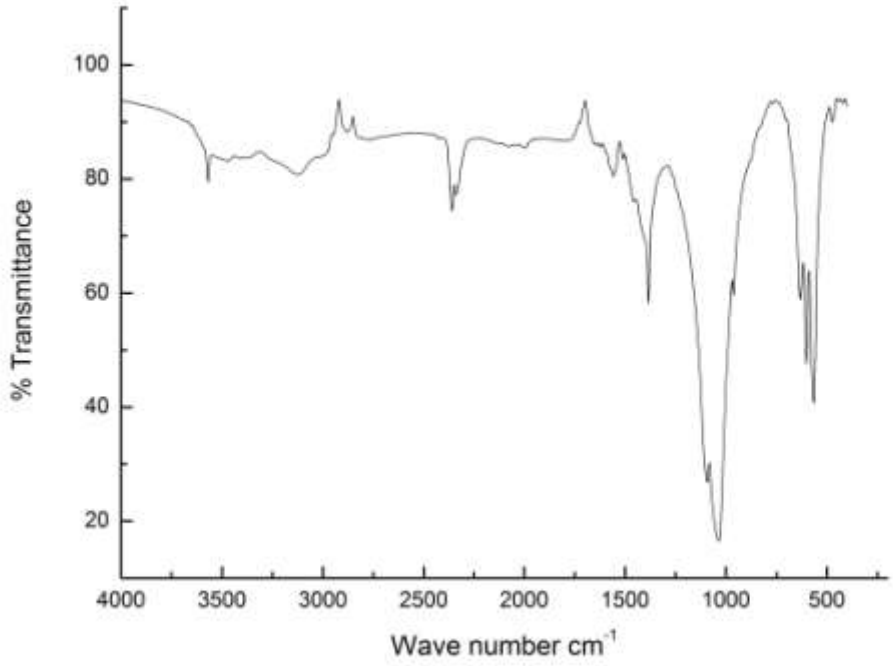

Fig 4.2b FTIR spectra of Mg-doped HAp

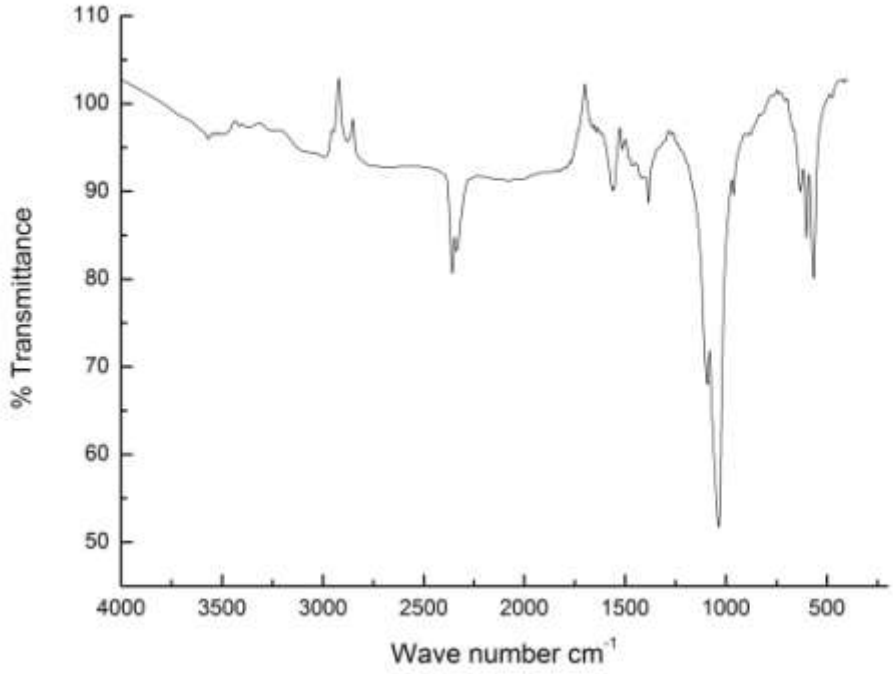

Fig 4.2c FTIR spectra of Si-doped HAp

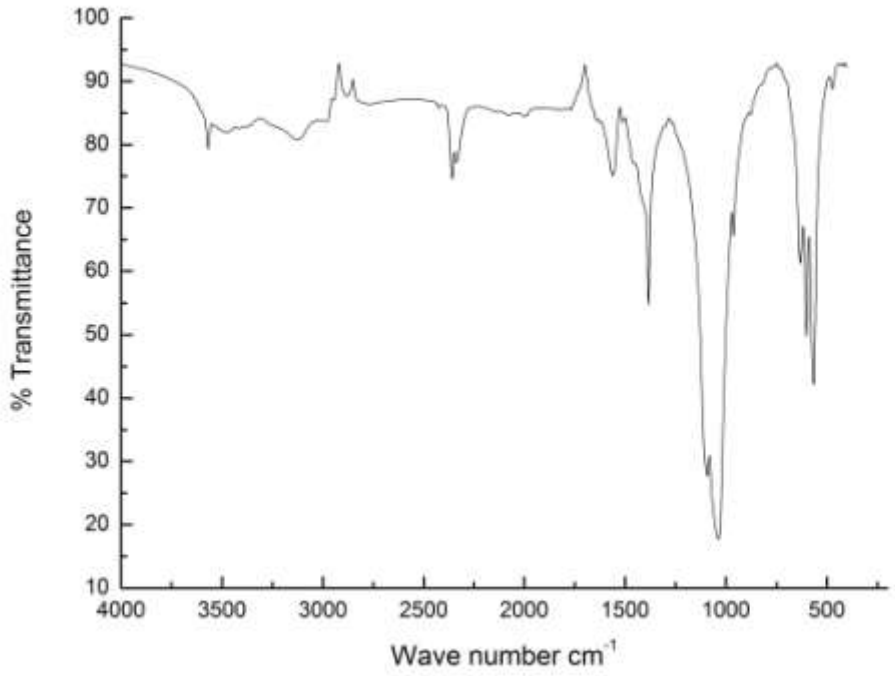

Fig 4.2d FTIR spectra of Zn-doped HAp

In the as synthesized pure and doped HA powders, a small peak at 1459 cm^{-1} corresponds to small amount of CO_3^{2-} present in the calcined powder. The band at 570, 606 cm^{-1} corresponds to the bending mode of $(PO_4)^{3-}$ and the strong absorption peaks at 1060 cm^{-1} and 963 cm^{-1} respectively are due to the vibration of $(PO_4)^{3-}$ group. The peak at 630 cm^{-1} is attributed to the hydroxyl vibration mode. The triplet at 570, 606 and 630 cm^{-1} along with the absorption band at 472 cm^{-1} indicates that phase pure HAp has been synthesized. This is further confirmed by the XRD analysis where no additional peak other than HAp was detected.

4.1.3 Particle Size Distribution

Average particle size values have been tabulated in Table 2. Pure HAp powder showed the lowest particle size of 1217nm whereas the Si-doped HAp showed the highest average particle size value of 1893nm.

Table 2: Average Particle size values of pure and doped HA powders.

Sample	Particle Size (nm)
HAp	1217
Si-HAp	1687
Mg-HAp	1893
Zn-HAp	1612

4.1.4 Microstructural study of sintered pure and doped HAp compacts

The SEM images of the samples were taken and microstructural analysis was done. As revealed from the SEM micrographs pure or undoped HAp sample was porous while the doped samples were highly dense with smaller grain size. Si and Zn doped sintered HAp compact showed finer microstructure, that is, smaller grain size, as compared to Mg-doped and pure HAp compact.

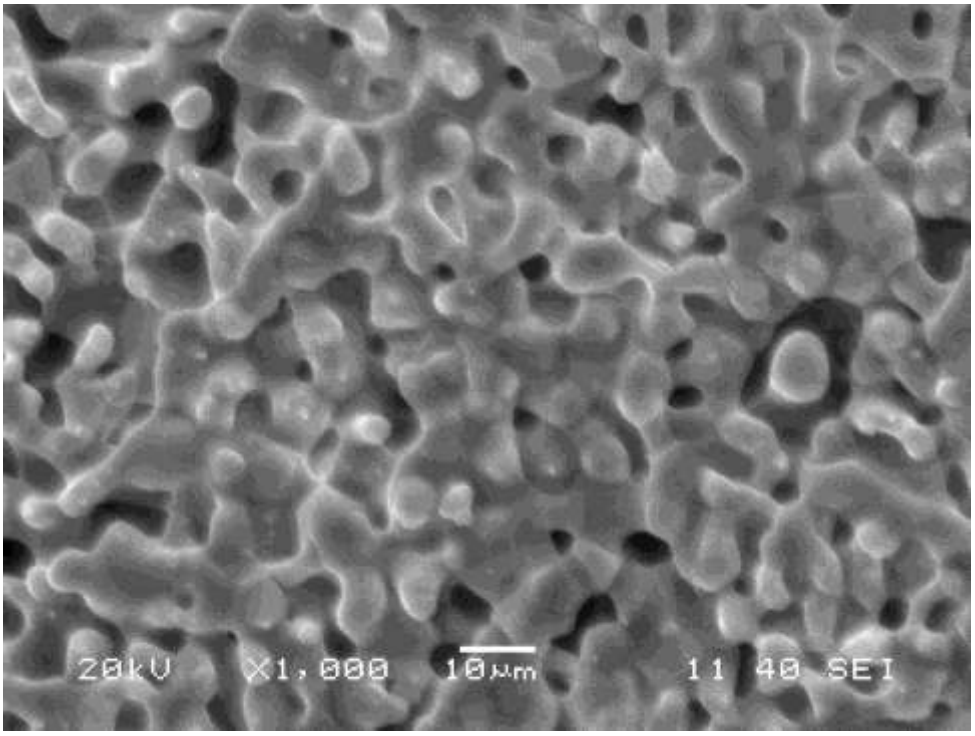

Fig 4.4a SEM micrograph of HAp pellet

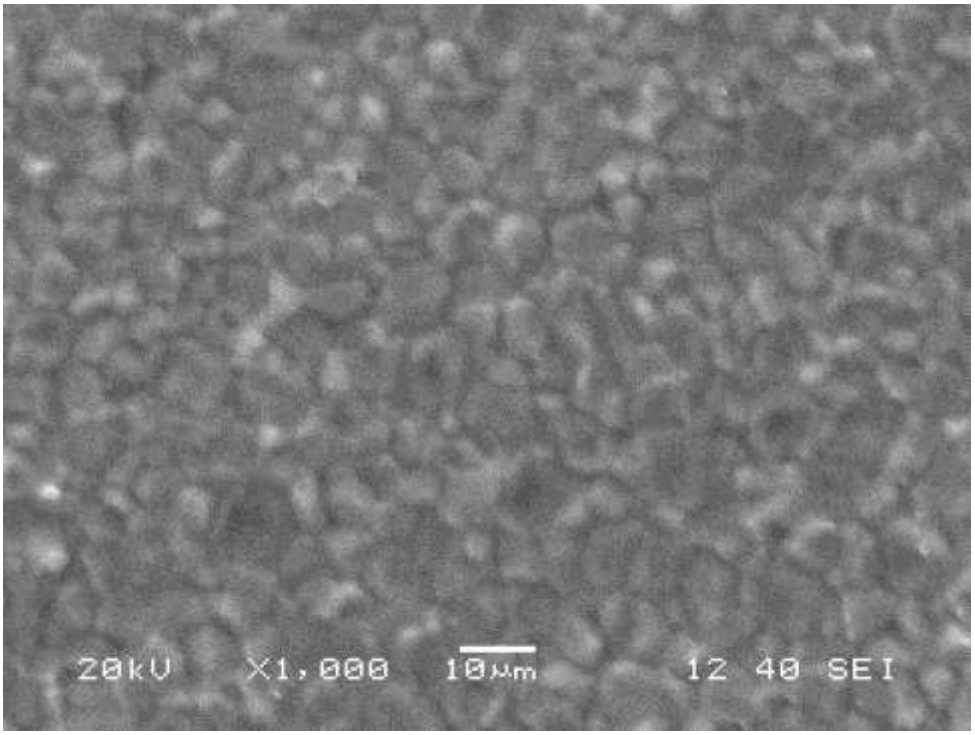

Fig 4.4b SEM micrograph of Mg-HAp pellet

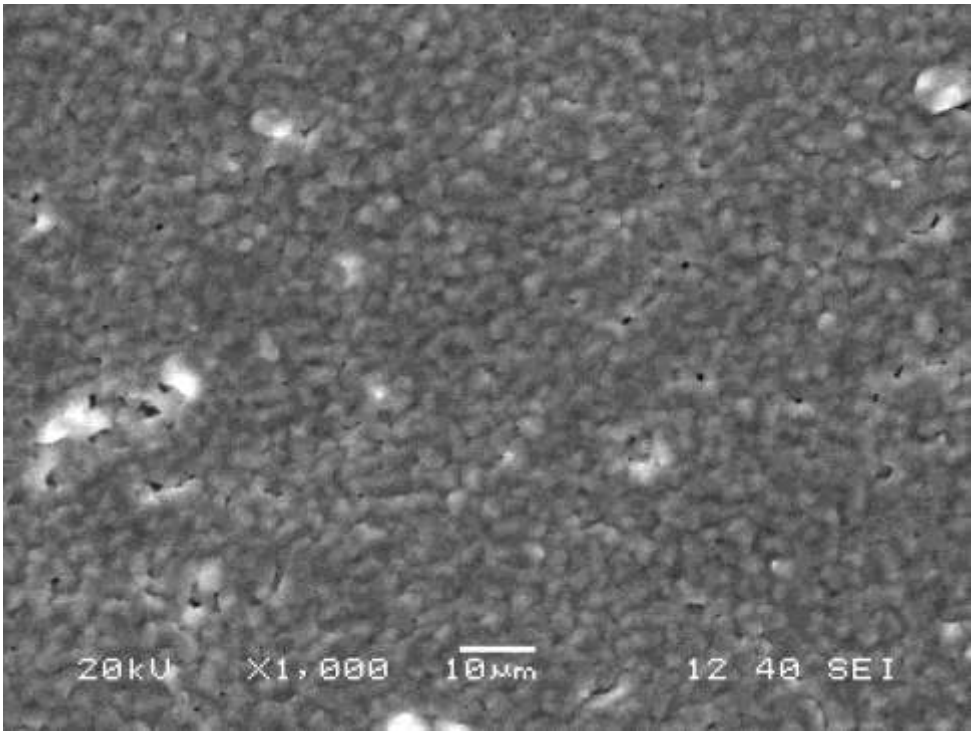

Fig 4.4c SEM micrograph of Si-HAp pellet

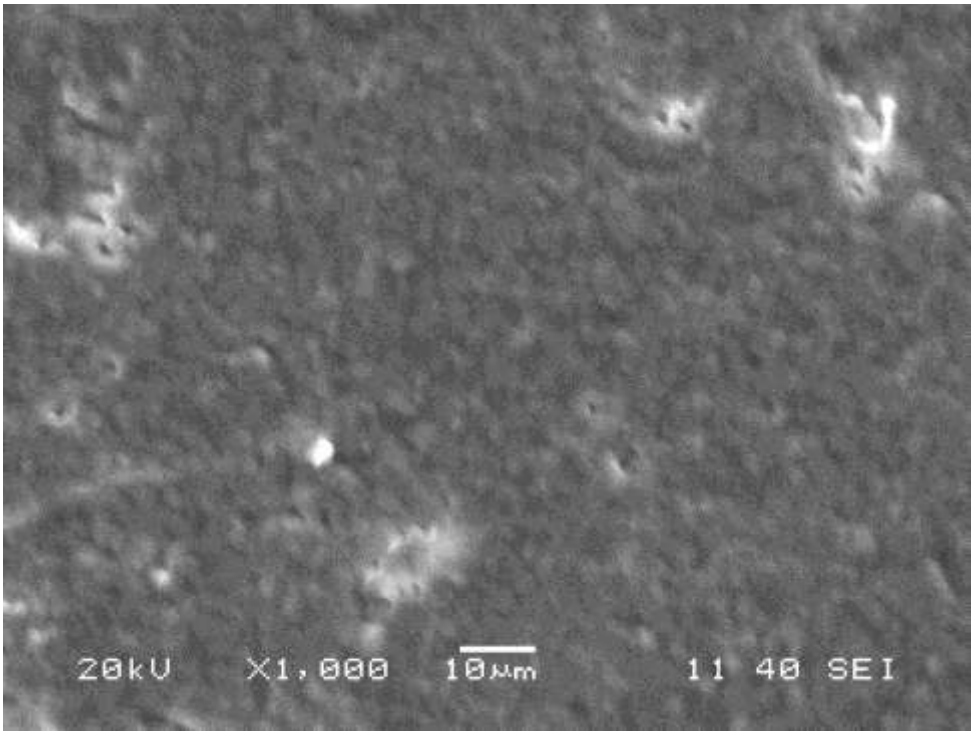

Fig 4.4d SEM micrograph of Zn-HAp pellet

4.1.5 Bulk Density

The average bulk density values of pure HAp and 2 mol% Mg-doped, Zn-doped and Si-doped HAp have been calculated. It was found that the density of the samples lie in the range of 2.29gram/cc to 2.96gram/cc. 2 mol% Mg doped compact showed the highest bulk density of 2.96 gm/cc. Doped HAp ceramics showed higher bulk density as compared to undoped one after sintering at 1250^{o}C for 4 hours. A comparison of bulk density values for different HAp based compacts are shown in figure 4.5 and the data tabulated in Table 3.

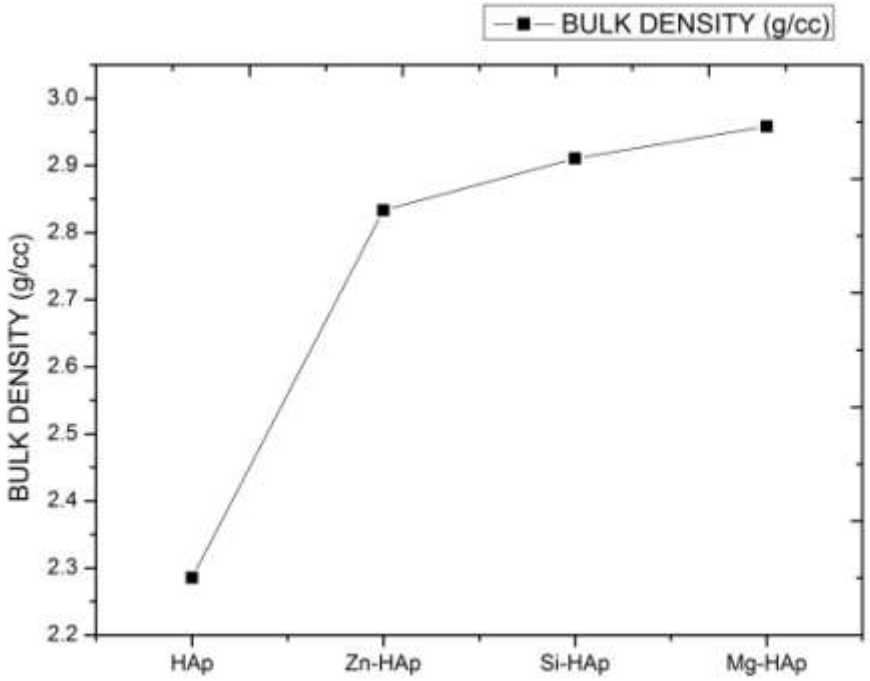

Fig 4.5 Comparison of bulk densities of sintered pure and doped HAp compacts

Table 3: Bulk density values of pure and doped HAp compacts sintered at1250^{o}C

Sample	Density(g/cc)
HAp	2.29
Zn-HAp	2.83
Si-HAp	2.91
Mg-HAp	2.96

4.1.6 Vickers Hardness Test

The Vickers Hardness values obtained in H_V, has been converted to GPa values and a graph has been plotted. It was observed that the hardness for the doped samples was greater than the hardness for the undoped HAp sample, with Zn-HAp having the highest indentation hardness value of 4.74 GPa.

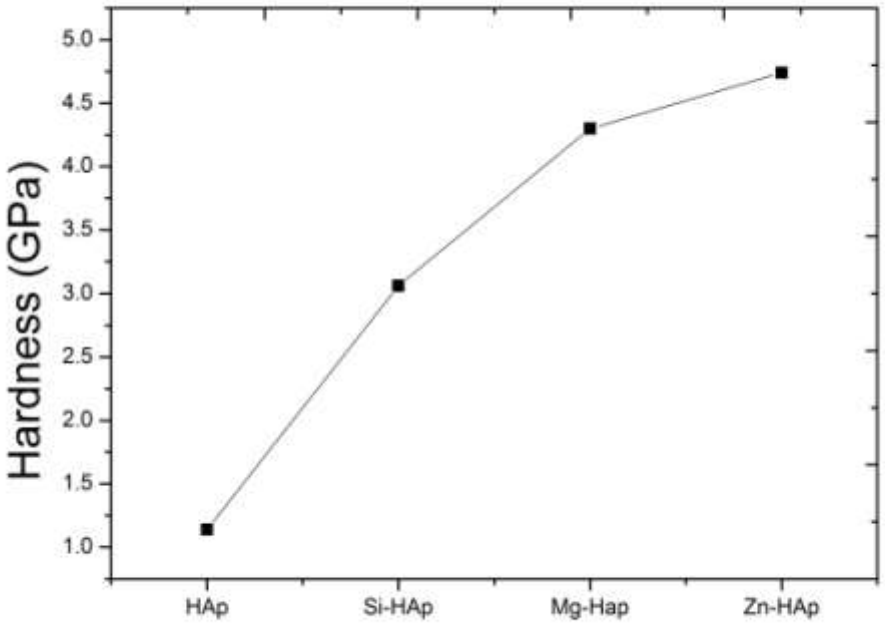

Fig 4.6 Hardness values of sintered pure and doped HAp compacts

Table 4: Indentation hardness values of pure and doped HAp compacts sintered at1250^{o}C

Sample	Hardness(GPa)
HAp	1.14
Si-HAp	3.06
Mg-HAp	4.30
Zn-HAp	4.74

4.1.7 Bi-Axial Flexural strength

The bi-axial flexural strength for the samples is calculated and a graph is plotted, showing the estimated values. It was observed that Si-HAp had the maximum strength of 20.8MPa.

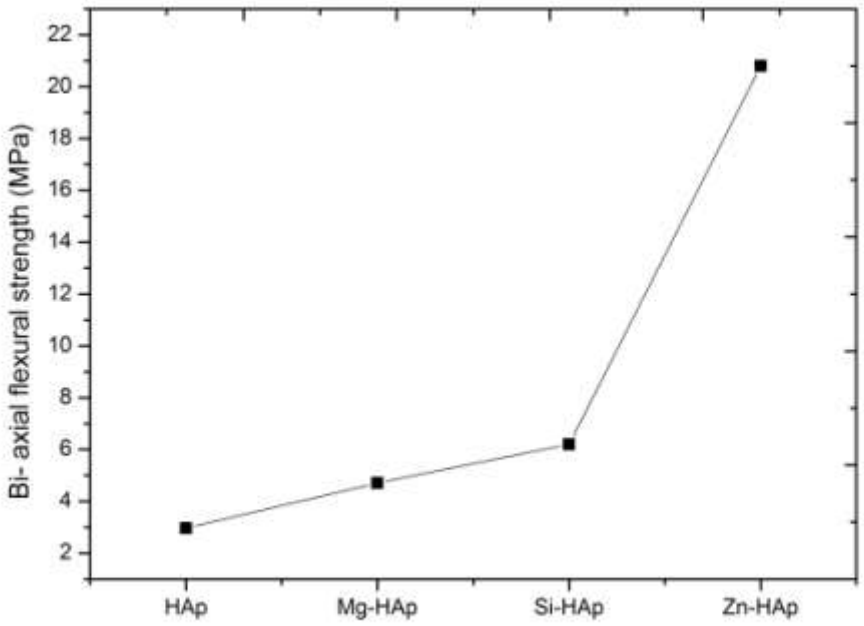

Fig 4.7 Bi-Axial Flexural Strength values of sintered pure and doped HAp compacts

Table 4: Flexural strength values of pure and doped HAp compacts sintered at1250^{o}C

Sample	Flexural Strength(MPa)
HAp	2.97
Mg-HAp	4.7
Si-HAp	6.2
Zn-HAp	20.8

4.1.8 Fracture Toughness

The fracture toughness was calculated from the observed respective crack lengths and Zn-HAp compacts showed the maximum fracture toughness of 1.49MPa.

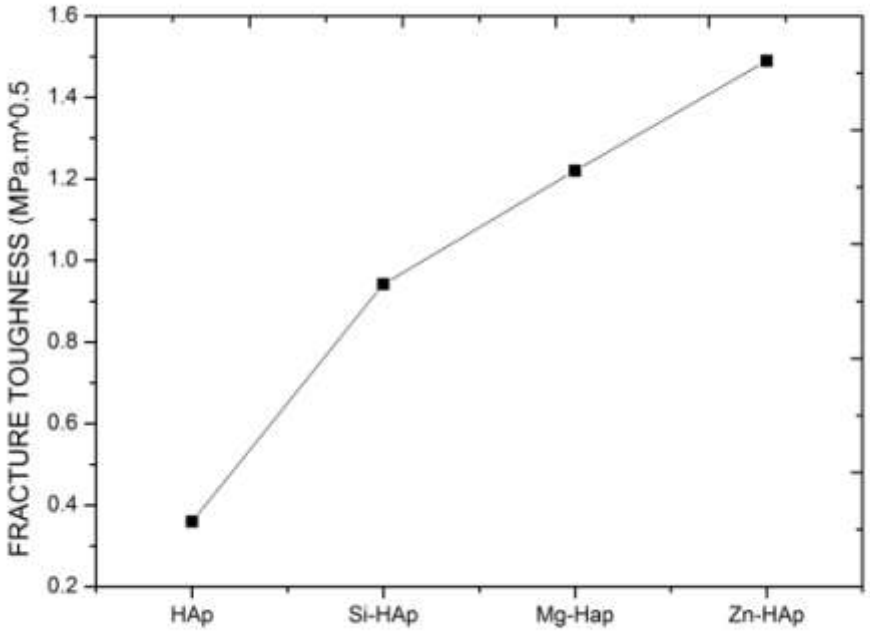

Fig 4.8 Comparison of fracture toughness values of sintered pure and doped HAp compacts

Table 3: Fracture Toughness values of pure and doped HAp compacts sintered at 1250^{o}C

Sample	**Fracture Toughness(MPa.m$^{1/2}$)**
HAp	0.36
Mg-HAp	0.942
Si-HAp	1.22
Zn-HAp	1.49

4.2 Discussion

Hydroxyapatite was precipitated out in the r4eaction mixture according to equation 1 as follows.

$$10\ Ca(NO_3)_2.4H_2O + 6NH_4H_2PO_4 + 14NH4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18NH_4NO_3 + 16H_2O \quad ....(1)$$

All the synthesized powders showed phase pure HA, which clearly demonstrated that Mg or Zn ions were structurally incorporated into the apatite crystals, they were not just absorbed on the surface of crystals. Doping with Si, Mg and Zn into HA was found to effectively suppress grain growth while good densification and phase stability was observed in all the sintered sample. Dopant incorporation into the crystal structure of HA enhanced the rate of diffusion at higher temperature and increased the sinterability of HA powders resulting in higher bulk density in doped HA compact as opposed to pure HA. The higher flexural strength in Zn doped HA can be attributed to its higher bulk density, lower flaw size and porosity in the sintered microstructure. It is clear that addition of Zn effectively suppressed grain growth in high quality HA samples and thus enhanced its mechanical properties significantly. The resulting ultrafine grains then are perhaps the most prominent factor that contributed to the higher fracture toughness of Zn-doped HA as suggested by Hall-Petch equation, $\sigma = \sigma_o + kd^{-1/2}$, where is the fracture strength, d is the grain size, k and σ_o are constants. The improved fracture toughness observed in the present work could also be associated with the suppression of microcracks that would be present in the HA structure due to thermal expansion anisotropy (TEA). Such microcracks can be avoided if the mean grain size of the sintered HA is less than some critical grain size for microcracking due to TEA. In the present work, dopants were found to be an effective grain growth inhibitor and as

such it is expected that finer grain size reduces the extent of micro-cracking resulting from TEA during the sintering of hydroxyapatite.

5. Conclusions

Pure hydroxyapatite and 2 mol% Mg, Si and Zn-doped hydroxyapatite compacts were processed and characterized. Phase pure hydroxyapatite powders were synthesized using wet chemical precipitation route after addition of 2 mol% Mg, Zn and Si into the precursor solution of Ca $(NO3)_2$ and $NH_4H_2PO_4$. Dopants had significant effect on densification behavior of sintered HA based compacts. Doped hydroxyapatite pellets sintered at 1250 C showed higher sintered density as compared to the undoped one. Mg doped HA compacts exhibited the highest bulk density of 2.96 gm/cc, whereas Zn-HAp showed the highest indentation hardness value of 4.74GPa, the highest bi-axial flexural strength value of 20.8MPa and the highest fracture toughness value of 1.49MPa. Zn and Si doped HA compacts showed finer microstructure as compared to Mg doped and pure HA compacts. The enhanced mechanical properties in Zn doped HA compacts can be attributed to its higher bulk density, finer microstructure and grain anisotropicity. In-vitro bioactivity study using osteoblast cell line would highlight the effect of doping on bioactivity of HAp compacts.

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